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(54)【発明の名称】 リチウム二次電池用正極活物質

(57)【特許請求の範囲】

【請求項1】リチウムまたはリチウム合金を負極活物質とするリチウム二次電池用正極活物質において、下記組成式(I)で表され、かつMn、Co、Niの原子比が、添付第1図に示す点A(x=0.95、y=0.05、z=0)、点B(x=0.05、y=0.95、z=0)、点C(x=0、y=0.95、z=0.05)、点D(x=0、y=0.66、z=0.34)、点E(x=0.66、y=0、z=0.34)、点F(x=0.95、y=0、z=0.05)で囲まれる範囲内(但し、z=0である範囲、およびy=0であって、xが0.75~0.95、かつzが0.05~0.25である範囲を除く)にある酸化物であって、酸素雰囲気下で焼成されてなるリチウム二次電池用正極活物質。

$\text{LiMn}_x\text{Co}_y\text{Ni}_z\text{O}_2$   
(x+y+z=1)

..... (I)

【発明の詳細な説明】

【産業上の利用分野】

本発明は、リチウムまたはリチウム合金を負極活物質とするリチウム二次電池用正極活物質に関する。

【従来の技術】

従来、リチウム二次電池などの非水電解質系二次電池の正極活物質として、例えば五酸化バナジウムおよび超電力の低い二硫化チタンや、そのほか電子導電性が比較的低い二酸化マンガンなどが使用されている。

【発明が解決しようとする課題】

ところで、前述したような五酸化バナジウムおよび二硫化チタンを正極活物質として使用した場合には、材料コストが嵩張って電池が高価となったり、二硫化チタンのように超電力が低くて電池特性上も好ましくないため、通常、安価で良好な超電力が得られる前記二酸化マ

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## CLAIMS

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### (57) [Claim(s)]

[Claim 1] In the positive active material for lithium secondary batteries which uses a lithium or a lithium alloy as a negative-electrode active material The point A which it is expressed with the following empirical formula (I), and the atomic ratio of Mn, Co, and nickel shows in Fig. 1 of attachment ( $x=0.95$ ,  $y=0.05$ ,  $z=0$ ) Point B ( $x=0.05$ ,  $y=0.95$ ,  $z=0$ ), Point C ( $x=0$ ,  $y=0.95$ ,  $z=0.05$ ) Point D ( $x=0$ ,  $y=0.66$ ,  $z=0.34$ ), Point E ( $x=0.66$ ,  $y=0$ ,  $z=0.34$ ) Within the limits surrounded at Point F ( $x=0.95$ ,  $y=0$ ,  $z=0.05$ ) Positive active material for lithium secondary batteries which is the oxide which exists (removing [ however, ] the range) whose  $x$  is 0.75 to 0.95, and whose  $z$  it is the range which is  $z=0$ , and  $y=0$ , and is 0.05-0.25, and it comes to calcinate under an oxygen ambient atmosphere.



$$(x+y+z=1)$$

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

### [Industrial Application]

This invention relates to the positive active material for lithium secondary batteries which uses a lithium or a lithium alloy as a negative-electrode active material.

### [Description of the Prior Art]

Conventionally, in addition to this, vanadium pentoxide and the low 2 titanium sulfides of super-power, a manganese dioxide with comparatively low electronic conductivity, etc. are used as positive active material of nonaqueous electrolyte system rechargeable batteries, such as a lithium secondary battery.

### [Problem(s) to be Solved by the Invention]

By the way, when vanadium pentoxide and 2 titanium sulfides which were mentioned above are used as positive active material, ingredient cost is bulky, and a cell becomes expensive, or since super-power is low and a \*\*\*\* cell property top does not have it, either, said manganese dioxide from which cheap and usually good super-power is obtained is used widely like 2 titanium sulfides. [ desirable ]

However, as the positive active material of this manganese dioxide was mentioned above, since electronic conductivity was comparatively low, the internal resistance of a cell became high, the electrode reaction ( $\text{MnO}_2 + \text{Li}^{++} + \text{e}^{-} \rightarrow \text{LiMnO}_2$ ) in a positive electrode did not fully progress, but the utilization factor was falling.

This invention aims at offering the positive active material for lithium secondary batteries which can aim at fall of internal resistance, and improvement in a utilization factor by raising the electronic conductivity of the positive electrode containing manganese.

### [The means for solving a technical problem]

In the positive active material for lithium secondary batteries with which this invention uses a lithium or a lithium alloy as a negative-electrode active material The point A which it is expressed with the following empirical formula (I), and the atomic ratio of Mn, Co, and nickel shows in Fig. 1 of attachment ( $x=0.95$ ,  $y=0.05$ ,  $z=0$ ) Point B ( $x=0.05$ ,

0.05, y= 0.95, z= 0), Point C (x= 0, y= 0.95, z= 0.05) Point D (x= 0, y= 0.66, z= 0.34), Point E (x= 0.66, y= 0, z= 0.34) Within the limits surrounded at Point F (x= 0.95, y= 0, z= 0.05) It is the oxide which exists (removing [ however, ] the range) whose x is 0.75 to 0.95, and whose z it is the range which is z= 0, and y= 0, and is 0.05-0.25, and the positive active material for lithium secondary batteries which it comes to calcinate under an oxygen ambient atmosphere is offered.

$\text{LiMnxCoyNizO}_2$  .... (I)

( $x+y+z=1$ )

In the positive active material of this invention the atomic ratio of Mn, Co, and nickel If it is within limits (however, the range whose x is 0.75 to 0.95 and whose z it is the range which is z= 0, and y= 0, and is 0.05-0.25 is removed) surrounded by point A->B->C->D->E->F->A and Mn increases more than a Point A - F line top Since discharge capacity will fall remarkably if cycle stability will deteriorate remarkably if electrical conductivity falls, and it becomes a utilization factor equivalent to  $\text{MnO}_2$  and Co increases more than a point B-C line top, and nickel increases in number more than a Point D - E-lines top further, neither is desirable.

In this invention, the electronic conductivity of the positive electrode containing manganese can be raised by using the oxide of the atomic ratio of the range of said point A-F (however, the range whose x is 0.75 to 0.95 and whose z it is the range which is z= 0, and y= 0, and is 0.05-0.25 is removed), and, thereby, fall of the internal resistance of a lithium secondary battery and improvement in a utilization factor can be aimed at.

Although the particle size of positive active material is not necessarily restricted when producing a positive electrode using this positive active material, mean particle diameter can make the positive electrode of high performance by using a thing 5 micrometers or less. In this case, to these powder, addition mixing of the binders, such as electric conduction agents, such as acetylene black, and fluororesin powder, etc. is carried out, it \*\*\*\*\* by the organic solvent, and a positive electrode can be produced by the approach of rolling out and drying with a roll. In addition, the amount of mixing of an electric conduction agent can be made into 5 - 50 weight section, especially 7 - 10 weight section to the positive-active-material 100 weight section, and if it is in this invention, since the conductivity of the positive active material is good, it can lessen the amount of the electric conduction agent used. Moreover, as for the loadings of a binder, it is desirable to consider as 5 - 10 weight section to said positive-active-material 100 weight section.

The positive active material of this invention adds organic solvents, such as ethanol, into a lithium carbonate, manganese carbonate, and the mixture of cobalt carbonate, grinding means, such as a ball mill, can grind it, can be calcinated at the temperature of 750-950 degrees C under an oxygen ambient atmosphere after desiccation for about 2 to 6 hours, can add said organic solvent further, and can manufacture it by grinding and drying with a ball mill.

in addition, as an electrolyte of the non-drainage system used for the rechargeable battery using the positive active material of this invention Anythings can be used if it is the nonaqueous matter which can move in order that it may be chemically stable and a lithium ion may consider electrochemical reaction as positive active material to positive active material and a negative-electrode active material. It is the compound which becomes especially with the combination of a cation and an anion. As a cation, as  $\text{Li}^+$  and an example of an anion,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ , A halogenide anion of the halogen group

element of Va group element like SbF<sub>6</sub><sup>-</sup>, Although the compound which has anions, such as a halogen anion like I<sup>-</sup> (I<sub>3</sub><sup>-</sup>), Br<sup>-</sup>, and Cl<sup>-</sup>, a perchloric acid anion like ClO<sub>4</sub><sup>-</sup>, HF<sub>2</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and SCN<sup>-</sup>, can be mentioned, it is not necessarily limited to these anions. As an example of an electrolyte with such a cation and an anion, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiSbF<sub>6</sub>, LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiI, LiBr, LiCl, LiAlCl<sub>4</sub> and LiHF<sub>2</sub>, LiSCN, LiSO<sub>3</sub>CF<sub>3</sub>, etc. are mentioned.

Especially among these, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiSbF<sub>6</sub>, and LiSO<sub>3</sub>CF<sub>3</sub> are desirable.

In addition, although this nonaqueous electrolyte is usually used after the solvent has dissolved, and especially a solvent is not limited in this case, a polar large solvent is used comparatively good. Specifically Propylene carbonate, ethylene carbonate, a tetrahydrofuran, 2-methyl tetrahydrofuran, dioxolane, dioxane, dimethoxyethane, Lactone, such as glymes, such as diethylene-glycol wood ether, and r-BUCHIRORAKUTAN The ester of boric acid, such as phosphoric ester, such as triethyl phosphate, and boric-acid triethyl Nitril, such as sulfur compounds, such as a sulfolane and dimethyl sulfoxide, and an acetonitrile One sort or two sorts or more of mixture, such as amides, such as dimethylformamide and dimethylacetamide, a dimethyl sulfate, nitromethane, a nitrobenzene, and a dichloroethane, can be mentioned. Especially among these, one sort or two sorts or more of mixed solvents chosen from ethylene carbonate, propylene carbonate, butylene carbonate, a tetrahydrofuran, 2-methyl tetrahydrofuran, dimethoxyethane, dioxolane, and gamma-butyrolactone are suitable.

the organic solid electrolyte into which polymers, such as a phosphazene polymer which has the above-mentioned nonaqueous electrolyte in the isocyanate bridge formation object of polyethylene oxide, polypropylene oxide, and polyethylene oxide, and has ethyleneoxide oligomer in a side chain, were infiltrated as this nonaqueous electrolyte and Li<sub>3</sub> -- inorganic solid electrolytes, such as lithium glass, such as inorganic ion derivatives, such as N and LiBCl<sub>4</sub>, Li<sub>4</sub>SiO<sub>4</sub>, and Li<sub>3</sub>BO<sub>3</sub>, can also be used. [ furthermore, ]

The lithium secondary battery which used the positive active material of this invention is further explained to a detail with reference to a drawing.

Namely, the lithium secondary battery which used the positive active material of this invention The inside of the positive-electrode case 10 of the carbon button form where opening 10a was sealed with the negative-electrode cover plate 20 as shown in Fig. 2 is divided with the separator 30 which has micropore. While the positive electrode 50 which has arranged the positive-electrode charge collector 40 in the divided positive-electrode side space at the positive-electrode case 10 side is contained, the negative electrode 70 which has arranged the negative-electrode charge collector 60 in negative-electrode side space at the negative-electrode cover-plate 20 side is contained.

As a negative-electrode active material used for said negative electrode 70, the lithium alloy which emits [ occlusion and ] a lithium or a lithium is used, for example. In this case, although the metal of II a, II b, III a and IV a containing a lithium, and a V a group or two or more sorts of its alloys are usable as a lithium alloy, aluminum, In, Sn, Pb(s), Bi(s), Cd(s) and Zn containing especially a lithium, or two or more sorts of these alloys are desirable.

As said separator 30, by porosity, it can let the electrolytic solution pass or can contain, or it can carry out, for example, a nonwoven fabric, knitted fabrics, etc. made of synthetic

resin, such as polytetrafluoroethylene, and polypropylene, polyethylene, can be used. In addition, a sign 80 is insulating packing made from polyethylene which is attached around the inner skin of the positive-electrode case 10, and carries out insulating support of the negative-electrode cover plate 20.

[Example]

Hereafter, although the example of this invention is explained, this invention is not necessarily limited to this example.

Example 1 of a comparison Weighing capacity of Li<sub>2</sub>CO<sub>3</sub>, and MnCO<sub>3</sub> and CoCO<sub>3</sub> is carried out so that it may be set to Li:Mn:Co=1:0.5:0.5 by the atomic ratio. Add 25% of the weight of ethanol to this, and it mixes with a ball mill for 2 hours. After drying this the back, performing heat treatment of 2 hours at 750 degrees C into the oxygen ambient atmosphere and then adding 50% of the weight of ethanol again, powdered positive active material (LiMn<sub>1/2</sub>Co<sub>1/2</sub>O<sub>2</sub>) was obtained by grinding with a ball mill for 12 hours.

The obtained positive active material had the carrier concentration lower than the example 1 later mentioned as shown in line I of the graph of Fig. 3 in bulk, consequently about one-example high conductivity was not obtained. Moreover, it is what is inferior to an example 1 also about the electronic conductivity of a positive electrode. The internal resistance of a lithium secondary battery became higher, and the about one-example utilization factor was not acquired. In this positive-active-material 100 weight section Acetylene black is used as 10 weight sections and adhesives as an electric conduction agent. A Teflon binder Ten weight sections, in addition after mixing, It kneaded by the ethanol which is an organic solvent, and rolled out to about 200 micrometers with the reduction roll, and after carrying out the vacuum drying at 150 degrees C, what was pierced in the predetermined path was used as the positive electrode.

The negative electrode stuck the lithium to the aluminum plate pierced in the predetermined dimension by pressure, and what carried out the solvent of LiClO<sub>4</sub> to the solvent of propylene carbonate and diethylene-glycol wood ether by one mol / \*\* was used for it as the electrolytic solution, using what carried out ARUNIUMU-lithium alloying in the electrolytic solution, and it assembled the cell shown in Fig. 1 .

In this cell, in 5mA of charge discharge, charge and discharge were repeated by discharge-final-voltage 2V and charge termination electrical-potential-difference 4V, and 98 Ahr/kg and about one example high capacity was not obtained for the discharge capacity of 50 cycle eye.

Example 1 Positive active material (LiMn<sub>1/3</sub>Nickel<sub>1/6</sub>Co<sub>1/2</sub>O<sub>2</sub>) was obtained like the example 1 of a comparison except having used NiCO<sub>3</sub> and nickel(Li<sub>2</sub>CO<sub>3</sub> [ of Li:Mn:nickel:Co=1:0.33:0.17:0.5 ]3, MnCO<sub>3</sub> and CoCO<sub>3</sub>, OH)2.4H<sub>2</sub>O by the atomic ratio as an ingredient of positive active material.

As shown in line RO of the graph of Fig. 3 , the carrier concentration in bulk increased beyond the case of the example 1 of a comparison, higher conductivity was obtained, the improvement in electronic conductivity of a positive electrode was made by this, and the obtained positive active material was able to aim at fall of the above internal resistance, and improvement in a utilization factor from that of a lithium secondary battery.

Moreover, when the cell was formed like the case of the example 1 of a comparison using this positive active material, the result with a as good discharge capacity of this cell as 103 Ahr/kg was obtained.

example 2 of a comparison as the ingredient of positive active material -- an atomic ratio -- Li<sub>2</sub> of Li:Mn=1:1 -- positive active material (LiMnO<sub>2</sub>) was obtained like the example 1 of a comparison, and the example 2 except having used CO<sub>3</sub> and MnCO<sub>3</sub>.

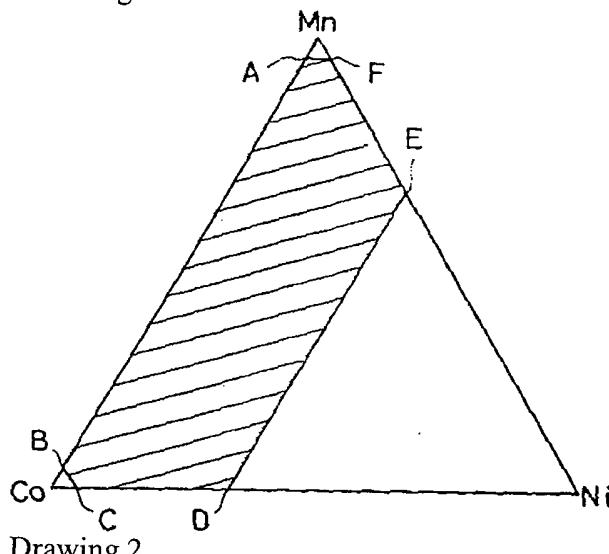
As shown to line Ha of the graph of Fig. 3, the carrier concentration in bulk fell, only low conductivity was obtained, but the electronic conductivity of a positive electrode was bad, the internal resistance of a lithium secondary battery became high, and the obtained positive active material had the low utilization factor.

Moreover, when the cell was formed like the case of the example 1 of a comparison, and an example 2 using this positive active material, as for the discharge capacity of this cell, the result of 90 Ahr/kg and low capacity was obtained.

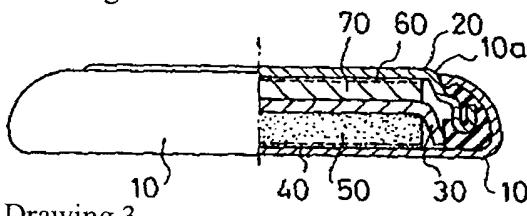
#### [Effect of the Invention]

Since this invention is such, the effectiveness that fall of internal resistance and improvement in a utilization factor can be aimed at is acquired by raising the electronic conductivity of the positive electrode containing manganese.

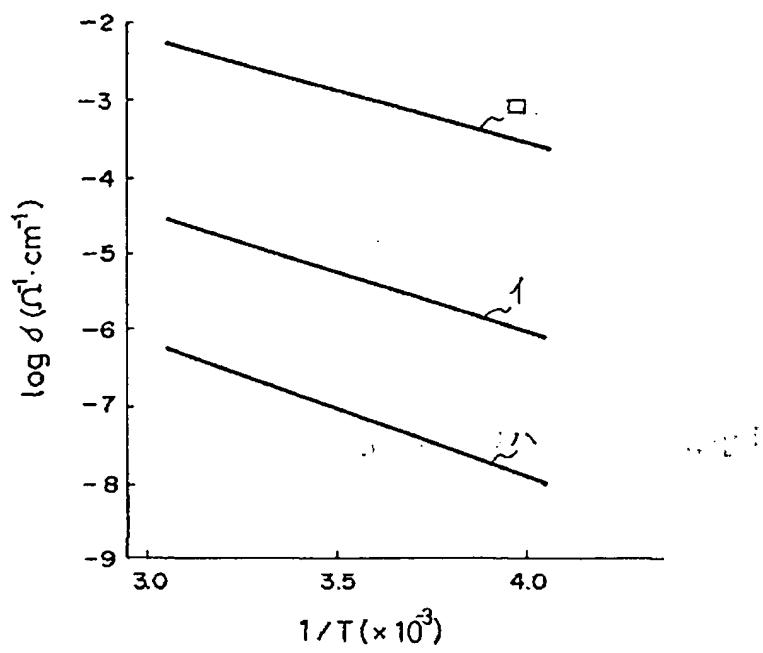
Drawing 1



Drawing 2



Drawing 3



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